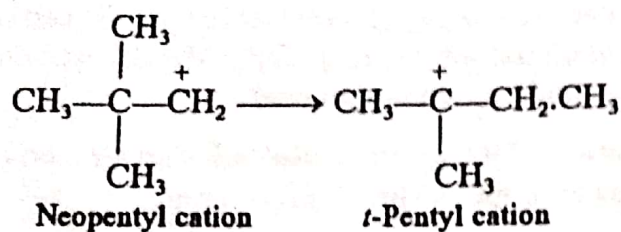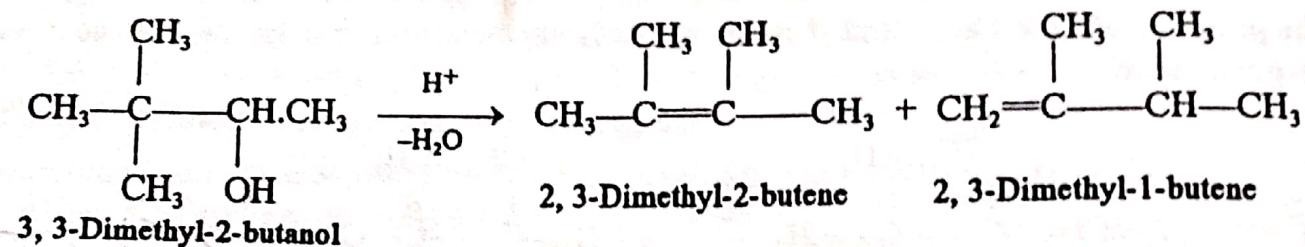compound *via* a ring closure reaction.

    2. Wagner-Meerwein rearrangements. One of the simplest systems in which carbon migrates with its bonding pair of electrons to an electron deficient carbon atom is the neopentyl cation.

Neopentyl cation   *t*-Pentyl cation

    Thus, all reactions in which neopentyl cation is formed as an intermediate produce compounds derived from the *t*-pentyl cation. For example, the acid catalyzed dehydration of 3, 3-dimethyl-2-butanol affords very little the expected compound 3, 3-dimethyl-1-butene, but yields mainly a mixture of 2, 3-dimethyl-2-butene and 2, 3-dimethyl-1-butene.


3, 3-Dimethyl-2-butanol   2, 3-Dimethyl-2-butene   2, 3-Dimethyl-1-butene

    Similarly,

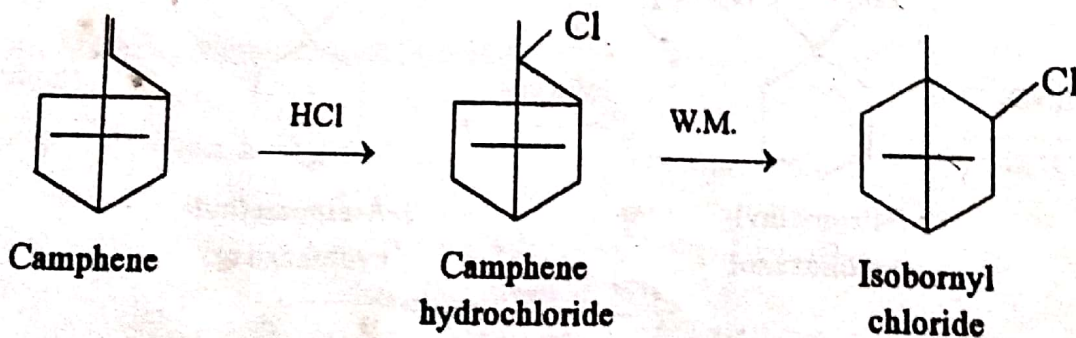Neopentyl alcohol   2-methylbutene-2   2-methylbutene-1
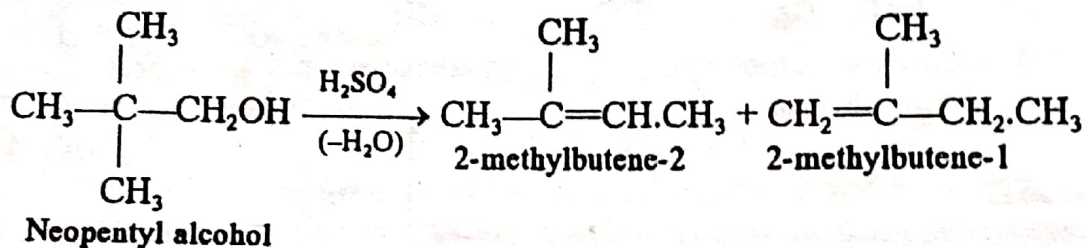
The rearrangement is also exhibited by alicyclic compounds, the important examples are give below.

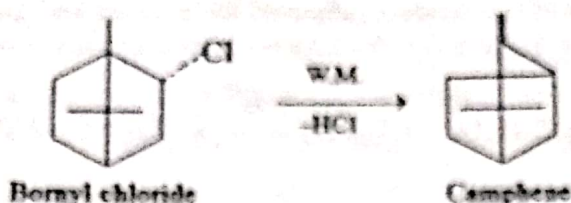**(a)** *Pinene hydrochloride to bornyl chloride.*

    α-Pinene   Pinene hydrochloride   Bornyl chloride

(b) *Camphene hydrochloride to isobornyl chloride.*
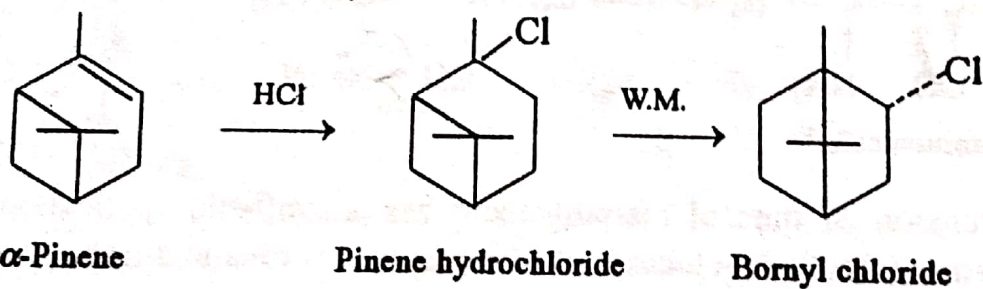
    Camphene   Camphene hydrochloride   Isobornyl chloride

(c) *Bornyl chloride to camphene.*

Bornyl chloride $\xrightarrow[\text{–HCl}]{\text{W.M.}}$ Camphene

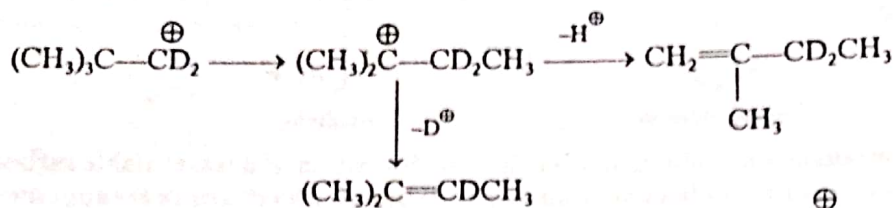Bornyl chloride   Camphene

Thus, the rearrangements which involve the transformation of a lesser stable carbonium ion into a more stable carbonium ion are collectively known as **Wagner-Meerwein rearrangements.**

Mechanism. The first stage of the reaction is the protonation of the hydroxyl group followed by the loss of a water molecule to yield a carbonium ion. Now since the so formed primary carbonium ion is relatively unstable, it rearranges itself to a more stable tertiary carbonium ion by the migration of a methyl group with its pair of bonding electrons. The tertiary carbonium ion may now be attacked by any nucleophilic species present in the reaction medium to form the substitution product or may be deprotonated form either the methylene group or a methyl group adjacent to the electron deficient carbon atom to give two olefins.
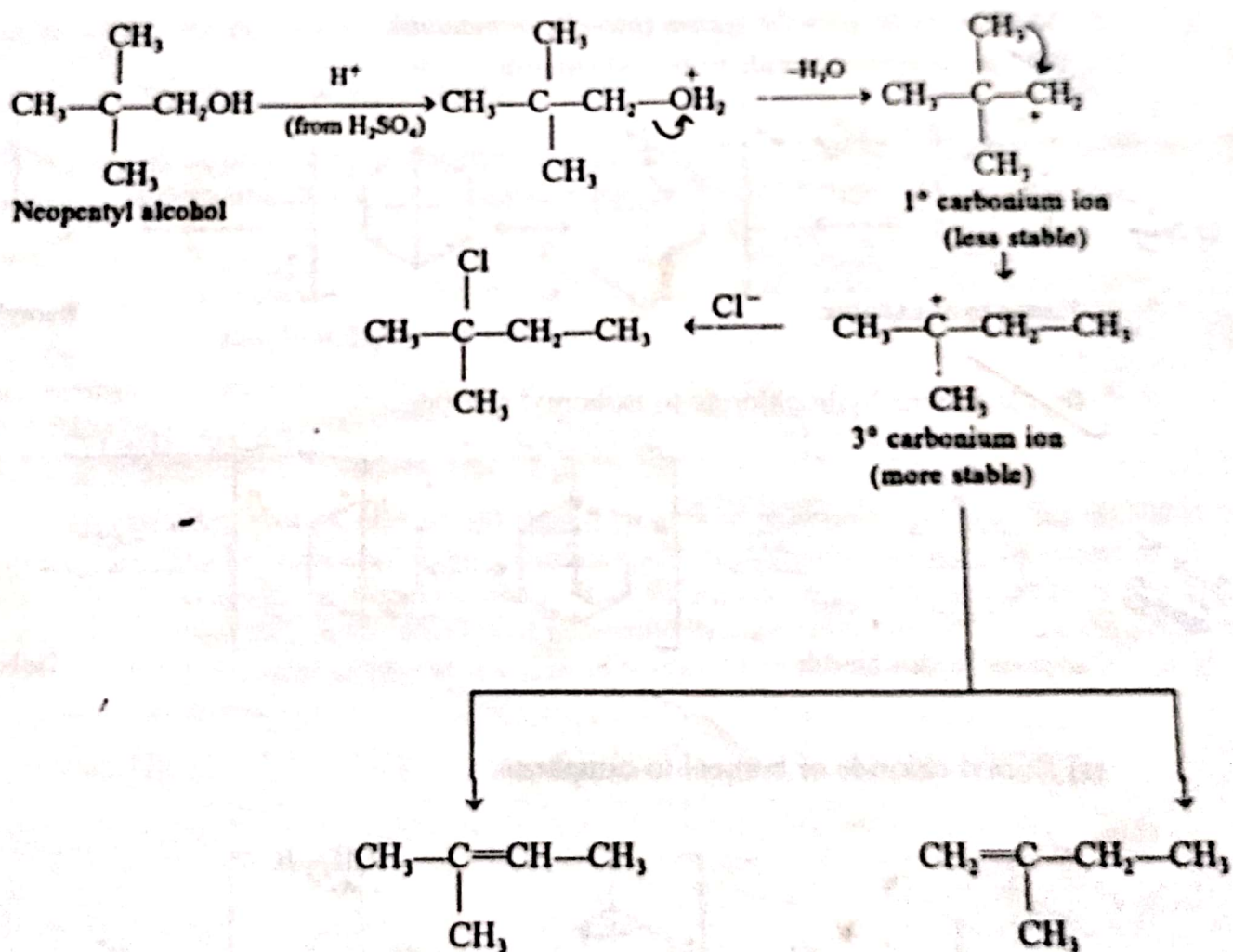

So in this case it is important to note that the driving force for the rearrangement resides in two factors, *viz.* (*i*) greater stability of the resulting tertiary carbonium ion than a primary carbonium ion, and (*ii*) steric repulsion between the three methyl groups in the starting material which is reduced when one of the methyl groups moves to the adjacent carbon. Rearrangement is especially favourable under these circumstances, and less so when a secondary carbonium ion is formed.

A valuable experiment has demonstrated that the carbonium ion from $(CH_3)_3C.CD_2OH$ rearranged primarily in a single way. Analysis of the product (alkenes) by infrared and nuclear magnetic resonance spectroscopy indicates the structure to have the deuterium located as shown below.

$$(CH_3)_3C\overset{\oplus}{-}CD_2 \longrightarrow (CH_3)_2\overset{\oplus}{C}-CD_2CH_3 \overset{-H^{\oplus}}{\longrightarrow} CH_2=\underset{\underset{CH_3}{|}}{C}-CD_2CH_3$$

$$\downarrow {-D^{\oplus}}$$

$$(CH_3)_2C=CDCH_3$$

This is compelling evidence to show that the carbonium ion $(CH_3)_3C\overset{\oplus}{C}D_2$ does not rearrange to $(CH_3)_2\overset{\oplus}{C}CH_2CD_2H$ since the latter ion would be expected to yield D on a terminal atom of the alkene.

$$CH_2=\underset{\underset{CH_3}{|}}{C}-CH_2-CD_2H \longleftarrow (CH_3)_2\overset{\oplus}{C}.CH_2CD_2H \longrightarrow (CH_3)_2C=CHCD_2H$$
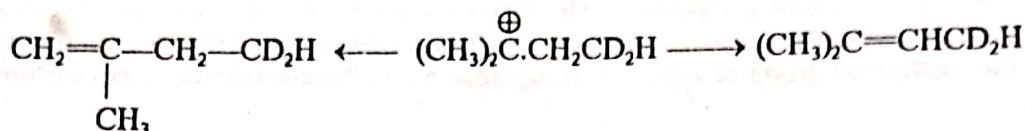
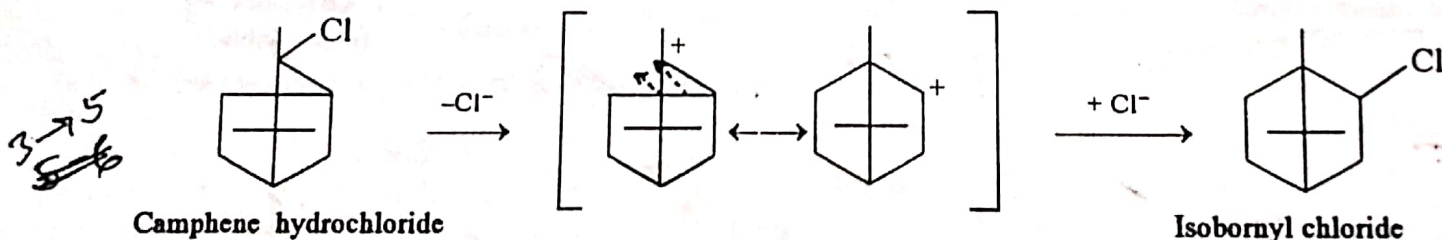*Mechanism in alicyclic system (bicyclic terpenoids).*

(a) Pinene hydrochloride to bornyl chloride.

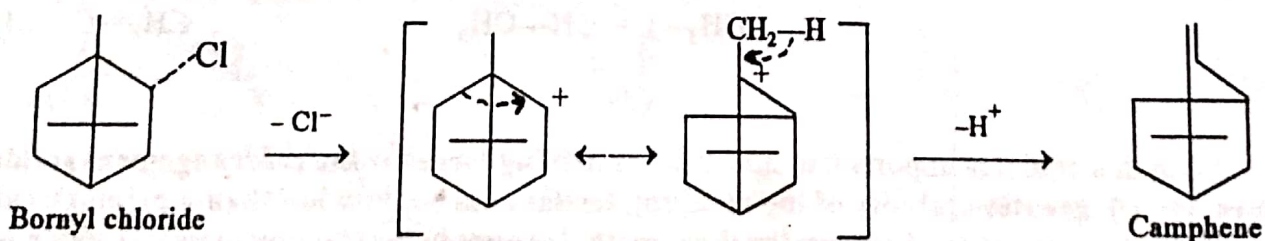Pinene hydrochloride   Bornyl chloride

(b) Camphene hydrochloride to isobornyl chloride.
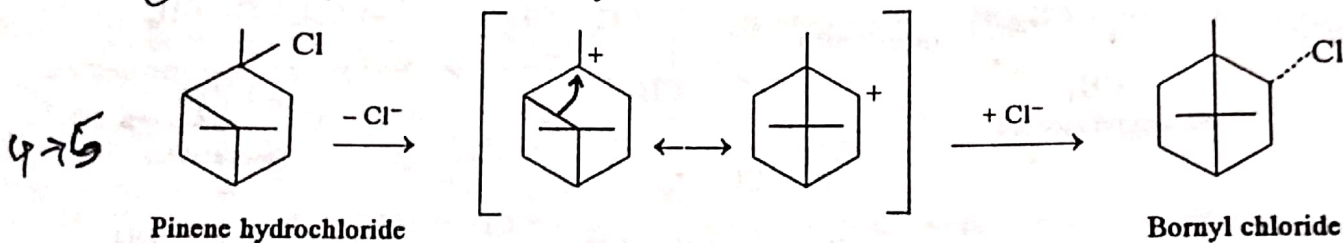
Camphene hydrochloride   Isobornyl chloride

(c) Bornyl chloride or borneol to camphene.

Bornyl chloride   Camphene

Note that in the first example the relief of strain (*i.e.*, the transformation of the strained four-membered ring into the less strained five membered analogue) provides a powerful driving force for rearrangement.