

Carbon to carbon migrations of R, H and Ar.

Wagner-Meerwein Rearrangement  $\rightarrow$  When alcohols are treated with acid, simple substitution or elimination usually accounts for most or all of the products. But in many cases, especially where two or three alkyl or aryl groups are on the  $\beta$ -carbon, some or all of the product is rearranged. Such changes in carbon skeleton, involving carbonium ions are known collectively as Wagner-Meerwein rearrangement. (i.e. not confined only to alcohols)

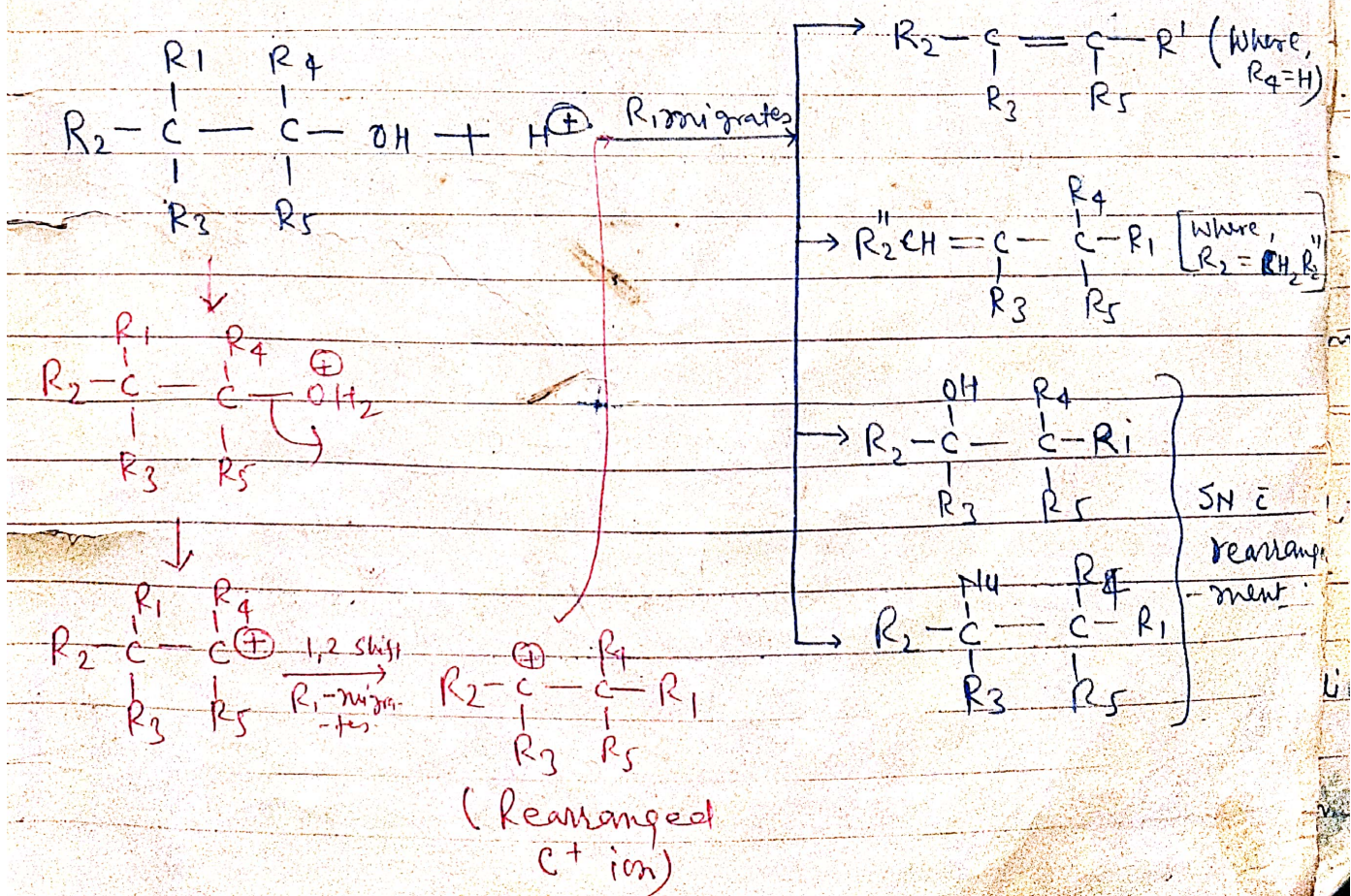
The term at present includes rearrangements involving many other leaving groups. A variety of substrates and electrophiles (to generate  $c^+$  ion) are involved. They all go via  $c^+$  ion routes and a number of these reactions are used for ring enlargements or contractions. These reactions of them have particular names.

The rearranged  $c^+$  ion, which is a direct product

~~of the rearrangement must stabilize itself by~~ —

- (a) the loss of a  $\beta$ -proton, so that the <sup>rearranged</sup> product is usually an olefin or
- (b) by direct interaction with a nucleophile. The latter is rather less common.

The general scheme is shown below: —

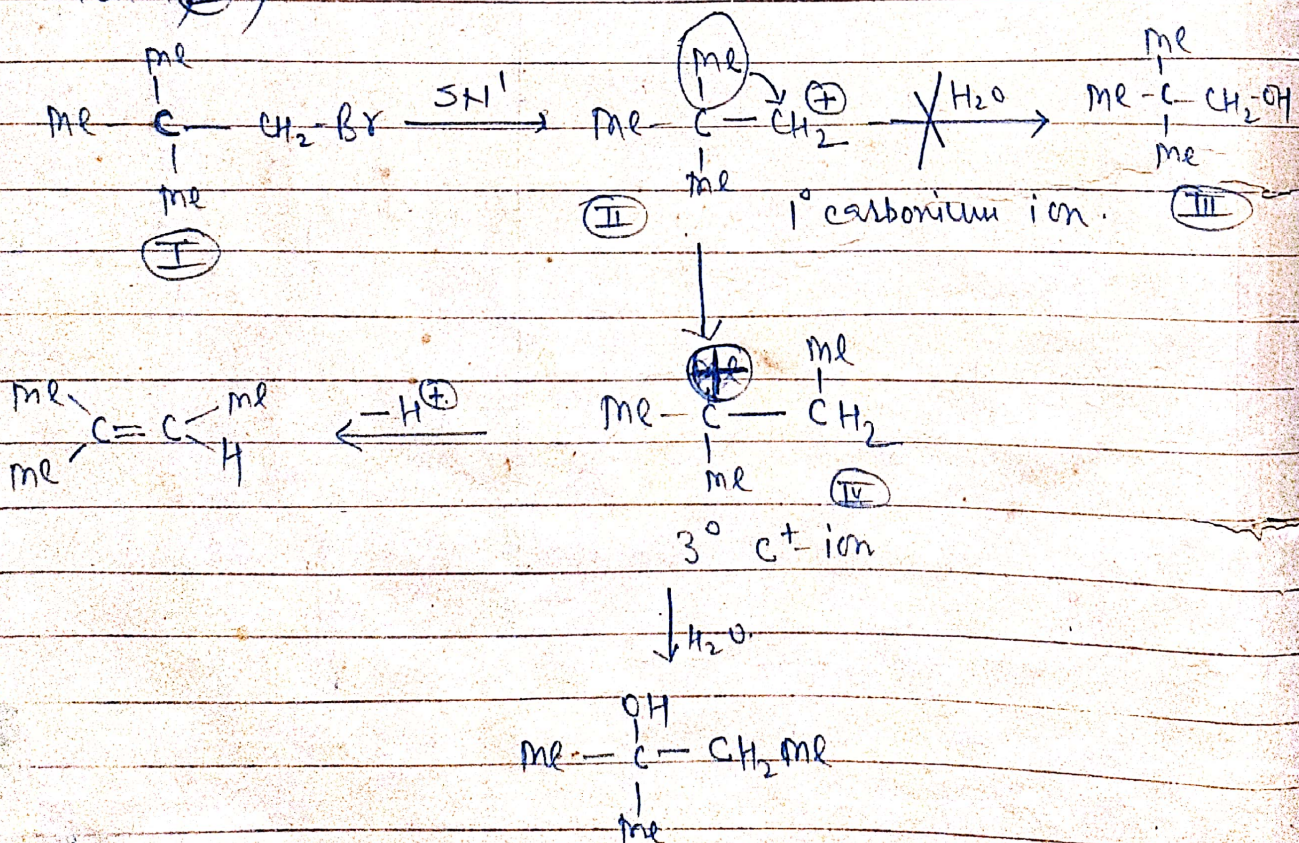


Evidently the proton lost may be  $R_3$  (if this is a hydrogen) or an  $\alpha$ -proton from  $R^2$  (if it has one). If there is a choice of protons, Saytzeff's rule governs the direction. (Sometimes a different  $\oplus$ ve group is lost instead of a proton.)

The nucleophile may be water, which is the original leaving group, so that the product is a rearranged alcohol or it may be some other species, which may be called Nu, as shown above.

Examples. This type of rearrangement is usually predominant in the neopentyl and neophyl types of substrates. With these types normal nucleophilic substitution is difficult (normal elimination is of course impossible). Under  $S_N2$  conditions substitution is extremely slow <sup>due to steric hindrance</sup> ~~under  $S_N1$  conditions carbocation ions are formed~~ which rapidly rearrange.

e.g., when 1-bromo-2,2-dimethylpropane (neopentyl bromide) is hydrolysed the product is 2-methyl propan-2-ol (II) and not the expected 2,2-dimethylpropan-1-ol (neopentyl alcohol) (I)

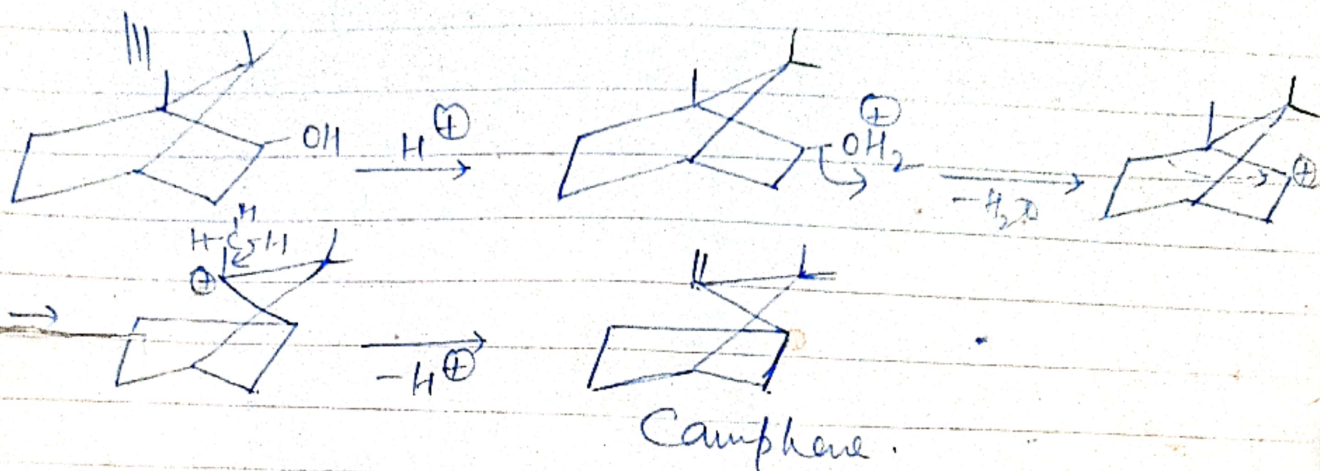
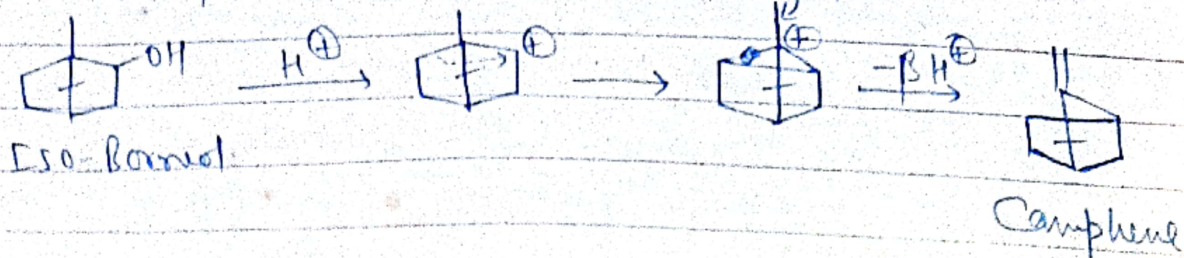


stability of the tertiary  $\text{c}^+$  ion (V) compared with

the initially formed primary one (II), provides the driving force for the necessary <sup>cc bond</sup> breaking involved in the migration of the methyl group.

The rearrangement is also exhibited by alicyclic compounds. The important examples are given below:

SX(1)



Other examples:

- (a)  $\alpha$ -Pinene to Borneol & Fenchyl alcohol
- (b) " " " Camphor

