Rearrangement

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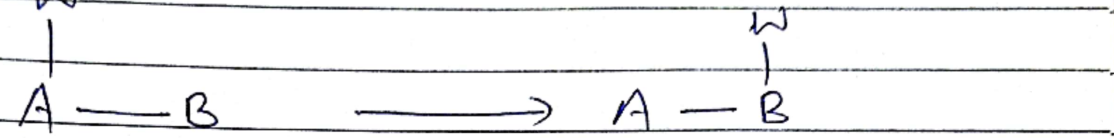
Introduction :- In a rearrangement reaction a group moves from an atom to another in the same molecule, hence the carbon skeleton in the product is changed. Thus molecular rearrangements may be defined as the reaction involving reshuffling of the sequence of atoms to form a new structure.

e.g.



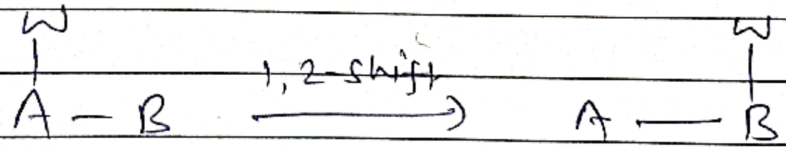
Substrate — Rearranged product

In this process :-

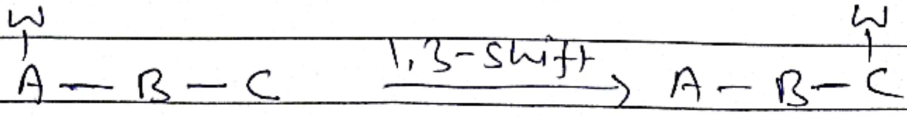
'A' is called – Migration origin
'W' is called – Migrating group.
'B' is called – Migration terminal (i.e. where migration stops)

When the migration involves a shift of migrating group from an atom to adjacent one, then it is called 1,2-shift (or whitmore shift), which is more common.

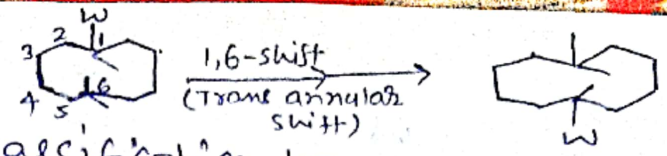
i.e,



Similarly



Even larger shifts are also possible but the longer shifts are not generally met with. However transannular shift (longer shift) are met with. →

e.g. 

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Classification :-

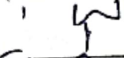
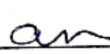
In a rearrangement, there are two possible modes of reaction :-

(i) Intramolecular :- Rearrangements within the same molecule is called intramolecular rearrangement, i.e, in this type the migrating group (W) goes from 'A' to 'B' in the same molecule. So in this type of rearrangement the migrating group does not become completely ~~free~~ detached from the system in which the rearrangement is occuring.

(ii) Intermolecular :- Those rearrangements, which involve the migration of the group amongst the molecules are called intermolecular. In this type of rearrangements migrating group is first detached and then reattached at another site (i.e, W becomes completely detached from 'A' and may end up on the 'B' atom of a different molecule).

Cross-over Experiment :-

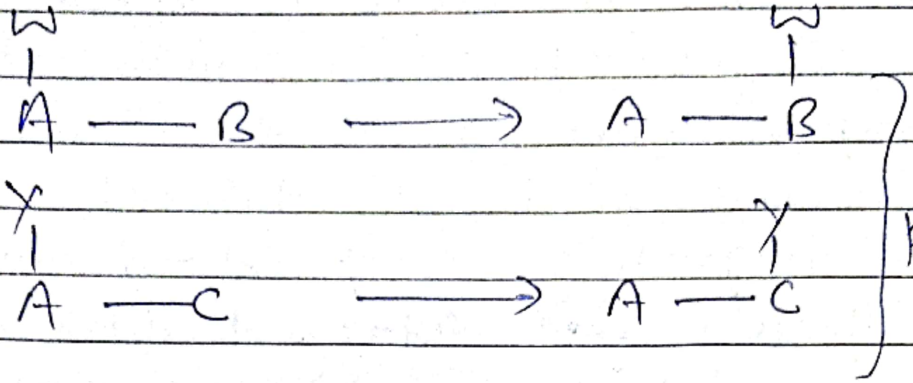
Distinction between intramolecular & intermolecular reassangement can be made by a simple cross-over experiment.

In this experiment, rearrangement is carried out on a mixture of say,  and 

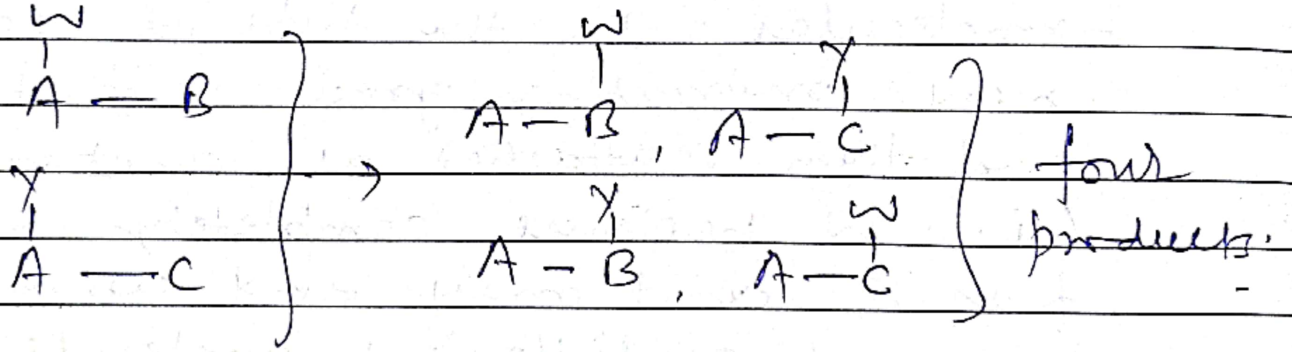
where 'Y' is closely related to 'W' (say ~~methyl or ethyl~~ and 'B' to 'C'.

In an Intramolecular

process only A—B and A—C will be recovered.



If the reaction is intermolecular, then together with these two, other two products will also be obtained as:-



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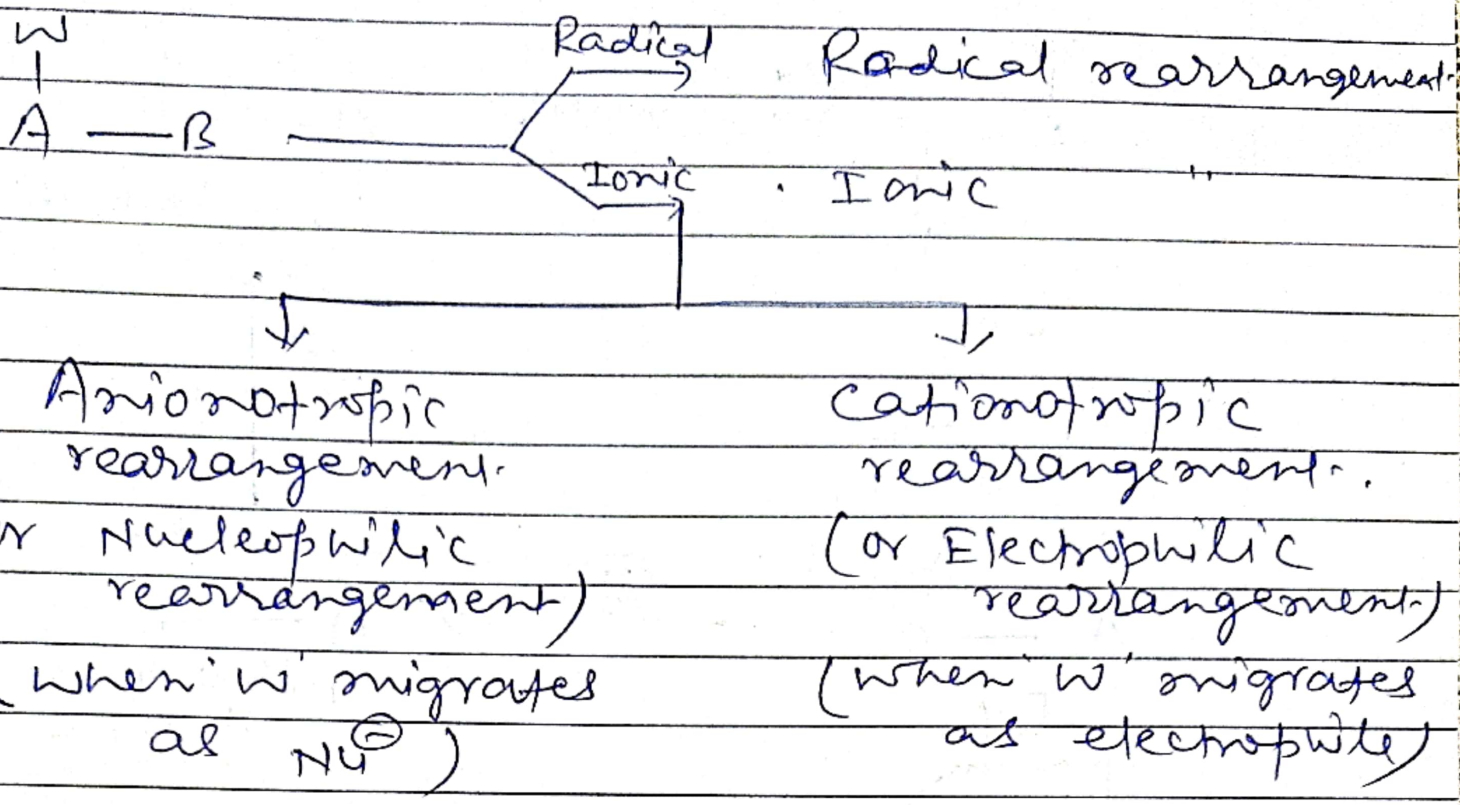
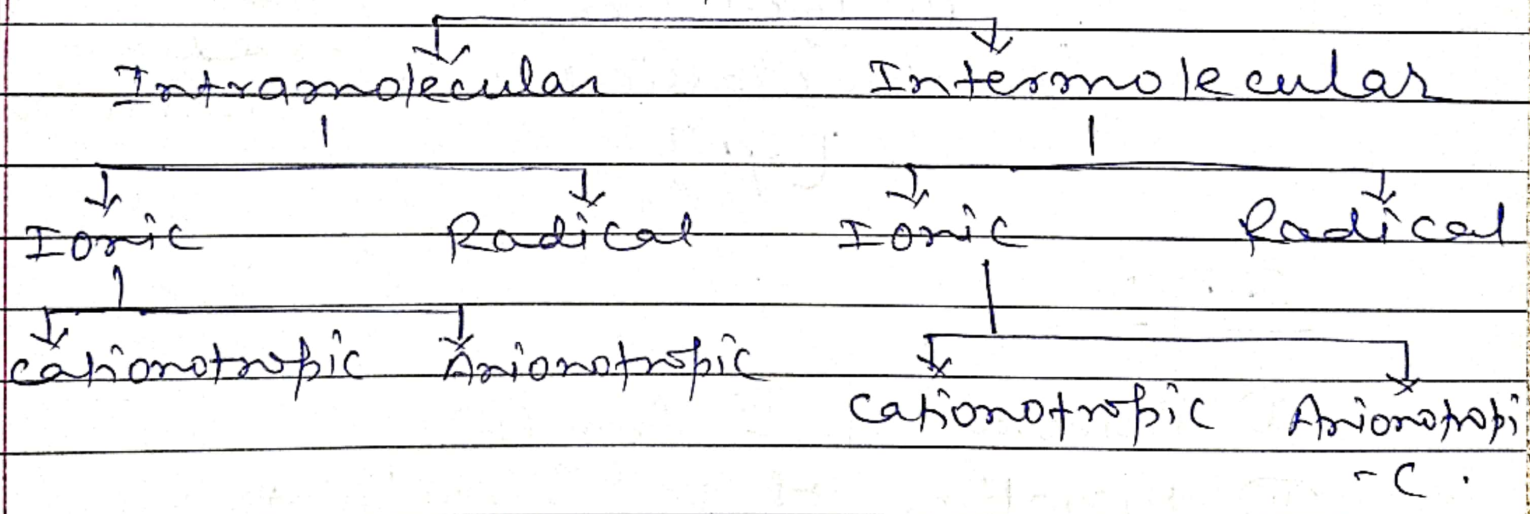
Mode of cleavage:

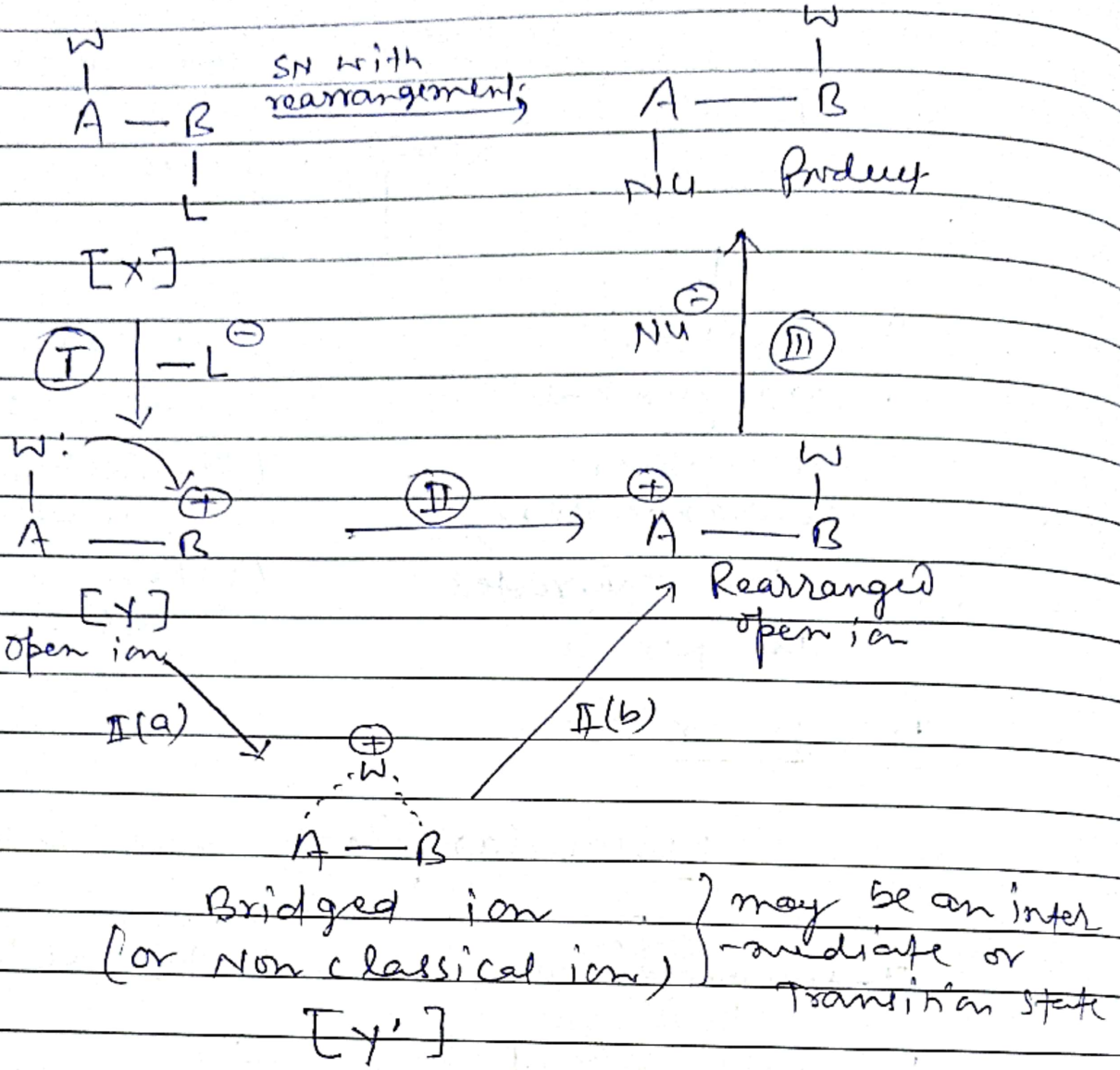


In general :-



However, there are some rearrangements which don't lead themselves to such neat categorisation in this manner. Among these are those involving cyclic transition states, like concerted reactions following orbital Symmetry rule.

General mode of Rearrangement



Steps :-

(I) Removal of $L^{\ominus}$ from (B)

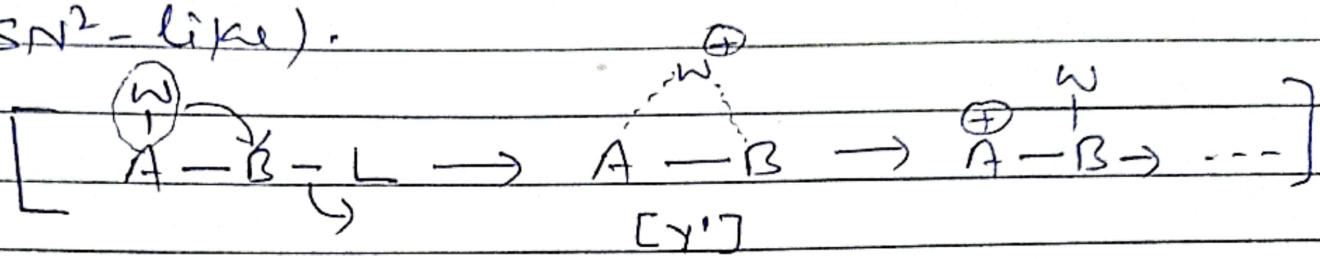
(II) Migration of 'W' from 'A' to 'B'

(III) Fresh electron deficient centre created at 'A' is electron satisfied by combination with a $Nu^{\ominus}$ or by the loss of β-proton. (More often the migration origin settles its charge by losing a β-proton).

These three steps may be discrete or some of these three are discrete and others are simultaneous or all three steps may be concerted. Thus following cases arise :—

(a) If there is racemisation at 'B' then step (I) is discrete (i.e, first step takes place before the second & that a carbonium ion carbon is present at 'B'. So with respect to 'B' there is a S_N1-type process).

(b) If there is inversion at 'B' then step (I) and (II) are synchronous (i.e, a carbonium ion is not an intermediate & the process is S_N2-like).



In this case participation by 'W' is assisting removal of 'L' in the same way that neighbouring groups do. (the only difference is that in the case of neighbouring grp mechanism of nucleophilic substitution 'W' never becomes detached from 'A', while in a rearrangement the bond between W & A is broken.) [Y'] may be a true intermediate or transition state, depending upon what migrates. However inversion of configuration at 'B' does not necessarily indicate an S_N2-process.

(c) Racemisation at 'A' indicates step II(b) is discrete

(d) Inversion at 'A' indicates (I) & (II) are synchronous.