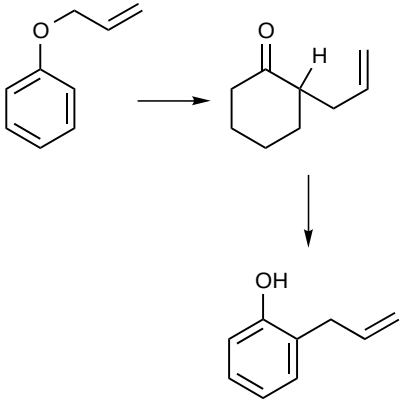
molecular rearrangement

The term is traditionally applied to any reaction that involves a change of connectivity (sometimes including hydrogen), and violates the so-called 'principle of minimum structural change'. According to this oversimplified principle, *chemical species* do not isomerize in the course of a *transformation*, e.g. *substitution*, or the change of a functional group of a chemical species into a different functional group is not expected to involve the making or breaking of more than the minimum number of bonds required to effect that transformation. For example, any new substituents are expected to enter the precise positions previously occupied by displaced groups.

The simplest type of rearrangement is an *intramolecular* reaction in which the product is isomeric with the reactant (one type of 'intramolecular isomerization'). An example is the first step of the Claisen rearrangement:



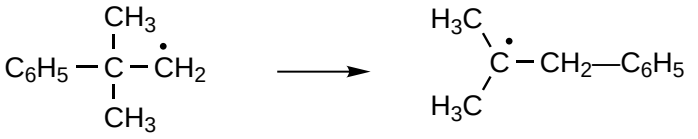
The definition of molecular rearrangement includes changes in which there is a *migration* of an atom or bond (unexpected on the basis of the principle of minimum structural change), as in the reaction:

$$CH_3CH_2CH_2Br + AgOAc \rightarrow (CH_3)_2CHOAc + AgBr$$

where the *rearrangement stage* can formally be represented as the '1,2-shift' of hydride between adjacent carbon atoms in the carbocation:

$$CH_3CH_2CH_2^+ \rightarrow CH_3CH^+CH_3$$

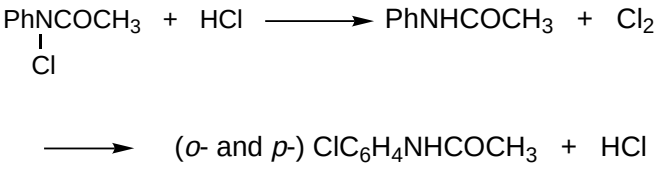
Such migrations occur also in radicals, e.g.:



The definition also includes reactions in which an *entering group* takes up a different position from the *leaving group*, with accompanying bond migration. An example of the latter type is the 'allylic rearrangement':

$$(CH_3)_2C{=}CHCH_2Br + OH^- \rightarrow (CH_3)_2C(OH)CH{=}CH_2 + Br^-$$

A distinction is made between 'intramolecular rearrangements' (or 'true molecular rearrangements') and '*intermolecular* rearrangements' (or 'apparent rearrangements'). In the former case the atoms and groups that are common to a reactant and a product never separate into independent fragments during the rearrangement stage (i.e. the change is intramolecular), whereas in an 'intermolecular rearrangement' a migrating group is completely free from the parent molecule and is re-attached to a different position in a subsequent step, as in the Orton reaction:



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