Equivalence Tests for Carbons and Protons

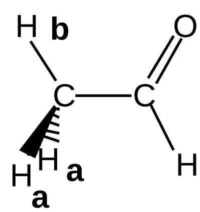
Chemical shift and non-equivalence:

Nuclei, in this case protons or carbons, are chemically non-equivalent if they experience chemically different environments. An important consequence of non-equivalence is that non-equivalent nuclei have different chemical shifts and appear as different signals in an NMR spectrum.

Simple equivalence tests that can be applied to carbons or hydrogens are presented below.

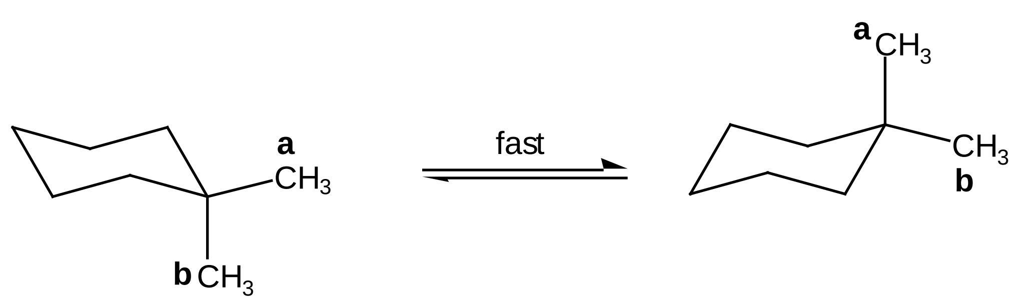
Interchange by rotation about single bonds:

Nuclei that can be interchanged by rotation about single bonds are equivalent. For example, despite the apparent non-equivalence of the methyl protons labeled **a** and **b** in acetaldehyde(ethanal), all three are interchanged by rotation about the C-C single bond. Thus, they are chemically equivalent and have the same chemical shift. Rotation about the single bond in ethanal



interchanges the methyl protons at a rate greater than 10^9 sec^{-1} making them "time-equivalent".

The rotation test can also be applied to carbons. Thus, the two methyls of 1,1-dimethylcyclohexane are chemically equivalent because the ring inversion process that interchanges them involves rotation about single bonds. It occurs at a rate of about 10^6 sec^{-1}.



By the rotation test, all six methyl hydrogens in 1,1-dimethylcyclohexane are chemically equivalent.

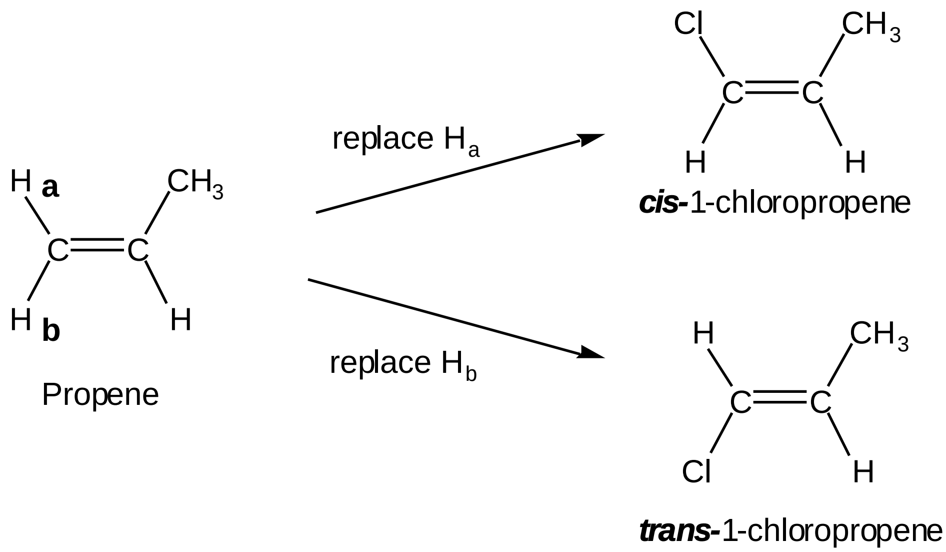
The atom replacement test:

Two atoms are each replaced in turn by a test atom:

- If the two atoms are chemically-equivalent, the same substitution product results.
- If the two atoms are chemically non-equivalent, different substitution products result.

In propene:

- Replacement of any of the three methyl protons of propene by chlorine leads to the same compound, 3-chloropropene. Thus, the three methyl protons are chemically-equivalent.
- Replacement of H_a and H_b leads to different compounds. Thus, H_a and H_b are chemically non-equivalent and will exhibit different NMR chemical shifts.

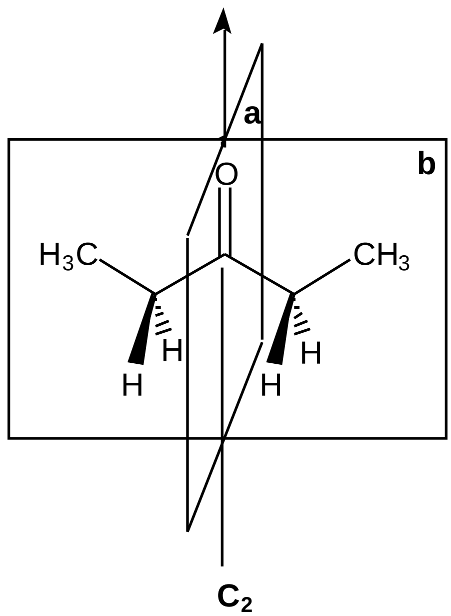


Interchange by symmetry operations:

- A symmetry operation is a movement of an object that leaves its appearance unchanged. Examples are reflection in a plane and rotation about an axis.

- If two atoms are interchanged by a symmetry operation, they are chemically equivalent.

An example is 3-pentanone (below):



- A 180^o rotation about the "two-fold" symmetry axis, $\mathbf{C_2}$, interchanges the methyl groups. Thus, all six methyl protons are equivalent as are the two methyl carbons.

- Reflection in symmetry plane **a** interchanges the "top" methylene protons and interchanges the "bottom" methylene protons.

- Reflection in symmetry plane **b** interchanges the "top" and "bottom" protons within each methylene group.

- These two reflections demonstrate the chemical equivalence of all four methylene protons.

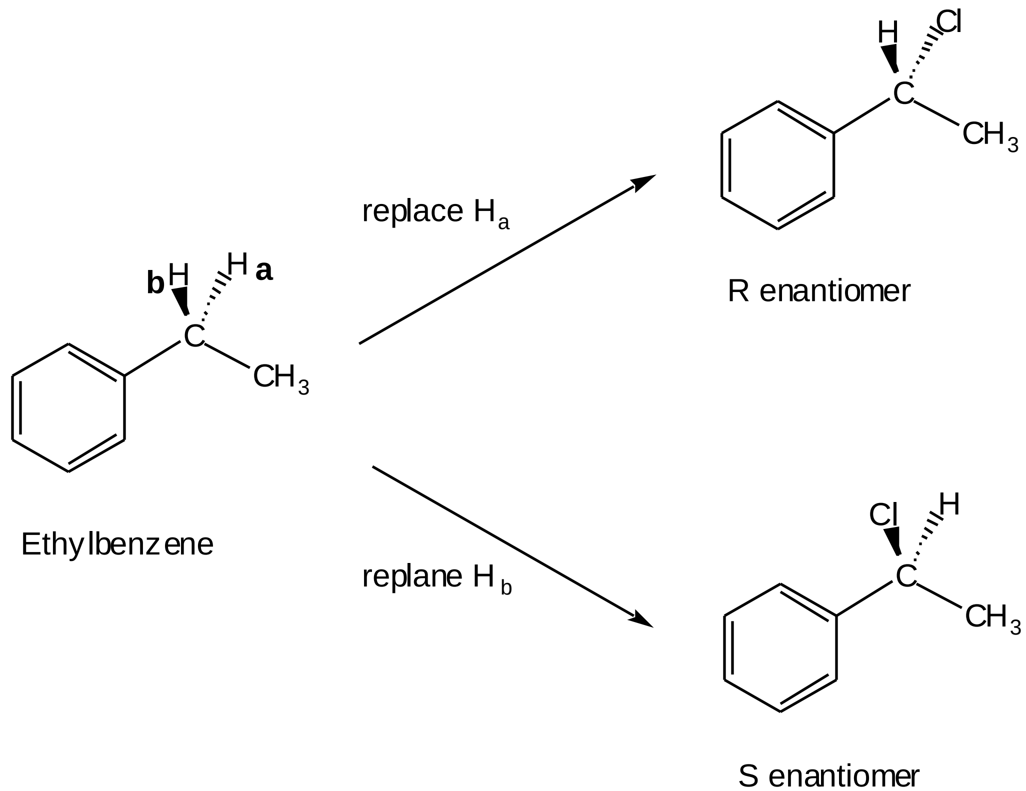
Thus, the proton-NMR spectrum of 3-pentanone exhibits signals with two different chemical shifts: methyl and methylene. The carbon-13 NMR spectrum exhibits three signals: methyl, methylene and carbonyl.

Diasteriotopic and enantiotopic atoms in NMR:

These are easily recognized using the substitution test.

- If the substitution products are diastereomers, as they are in the case of propene above, the two atoms are said to be **diastereotopic**. Thus, $H_{\mathbf{a}}$ and $H_{\mathbf{b}}$ of propene are diasteriotopic.
- Diasteriotopic atoms are chemically non-equivalent and have different chemical shifts.

- If the substitution products are enantiomers, as they are in the case of $H_{\mathbf{a}}$ and $H_{\mathbf{b}}$ in ethylbenzene, the two atoms are said to be **enantiotopic**.



Enantiotopic atoms are chemically equivalent and have the same chemical shift. (Note that protons **a** and **b** in ethylbenzene can be interchanged by reflection in a symmetry plane.)