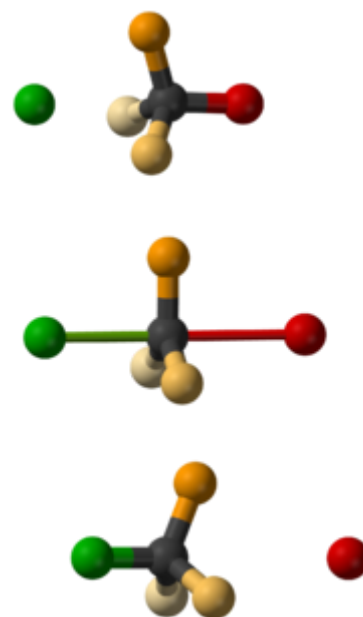


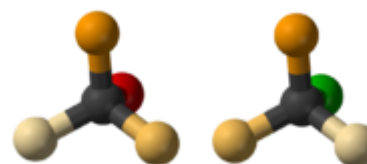
Walden inversion

Walden inversion is the inversion of a chiral center in a molecule in a chemical reaction. Since a molecule can form two enantiomers around a chiral center, the Walden inversion converts the configuration of the molecule from one enantiomeric form to the other. For example, in an S_N2 reaction, Walden inversion occurs at a tetrahedral carbon atom. It can be visualized by imagining an umbrella turned inside-out in a gale. In the Walden inversion, the backside attack by the nucleophile in an S_N2 reaction gives rise to a product whose configuration is opposite to the reactant. Therefore, during S_N2 reaction, 100% inversion of product takes place. This is known as Walden inversion.

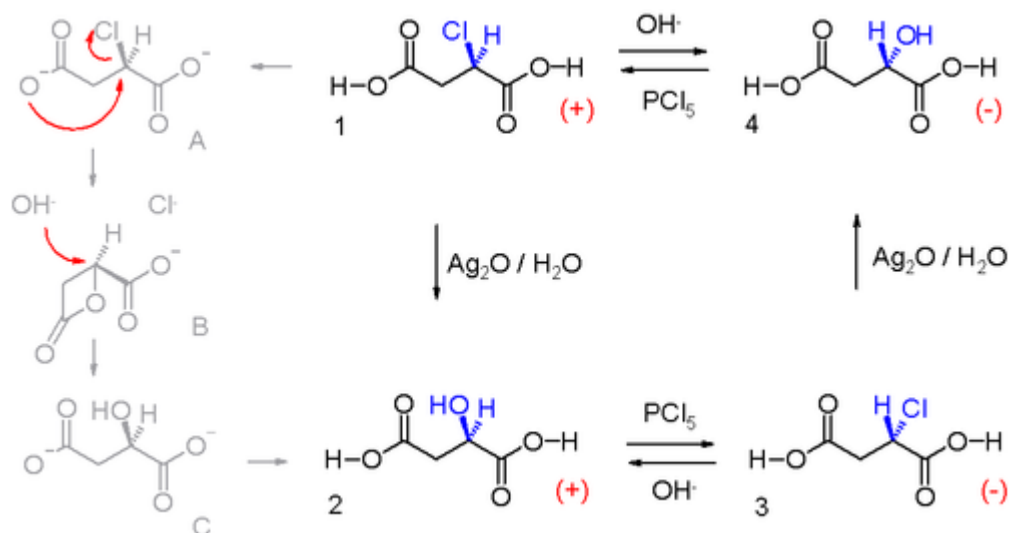
It was first observed by chemist Paul Walden in 1896. He was able to convert one enantiomer of a chemical compound into the other enantiomer and back again in a so-called **Walden cycle** which went like this: (+) chlorosuccinic acid (**1** in *scheme 1*) was converted to (+) malic acid **2** by action of silver oxide in water with retention of configuration, in the next step the hydroxyl group was replaced by chlorine to the other isomer of chlorosuccinic acid **3** by reaction with phosphorus pentachloride, a second reaction with silver oxide yielded (-) malic acid **4** and finally a second reaction with PCl₅ returned the cycle to its starting point.^[1]



Montage, using ball-and-stick models, of the three steps in an S_N2 reaction. The nucleophile is green, the leaving group is red and the three substituents are orange.



The S_N2 reaction causes inversion of stereochemical configuration, known as Walden inversion.



In this reaction, the silver oxide in the first step acts as a hydroxide donor while the silver ion plays no role in the reaction. The intermediates are the carboxyl dianion **A** which gives an intramolecular nucleophilic substitution by the β -carboxylate anion to produce a four-membered β -lactone ring **B**. The α -carboxyl group is also reactive but in silico data suggests that the transition state for the formation of the three-membered α -lactone is very high. A hydroxyl ion ring-opens the lactone to form the alcohol **C** and the net effect of two counts of inversion is retention of configuration.^[2]

See also

- Another demonstration of the Walden cycle in the Brook rearrangement.

References

- P. Walden (1896). "Ueber die gegenseitige Umwandlung optischer Antipoden" (<https://zenodo.org/record/1425826>). *Berichte der deutschen chemischen Gesellschaft*. **29** (1): 133–138. doi:10.1002/cber.18960290127 (<https://doi.org/10.1002%2Fcbcr.18960290127>).
- The Walden cycle revisited: a computational study of competitive ring closure to α - and β -lactones* J. Grant Buchanan, Richard A. Diggle, Giuseppe D. Ruggiero and Ian H. Williams *Chemical Communications*, **2006**, 1106 - 1108 Abstract.

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