Stereochemistry of addition reaction pdf

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In the previous post, we talked about the Markovnikov's rule and learned that in the addition reaction of HX to an unsymmetrical alkene, the H adds to the carbon that already has the greater number of hydrogen atoms. Or, looking from the perspective of the X group, we can say that the X atom (or group) adds to the carbon that already has the greater number of carbon atoms:This is the regiochemistry of the reaction as it shows why one regioisomer (constitutional isomer) is formed preferentially over the other one.Sometimes the addition to the alkene results in a product with one or two stereogenic (chirality) centers. The resulting product can be a mixture of stereoisomers which can be enantiomers or diastereomers.At this point, it might be a good idea to refresh the concepts of constitutional and stereoisomers by following the corresponding links above. Additionally, you want to check some practice problems identifying molecules as Enantiomers Diastereomers the Same or Constitutional.Without going too far, let's look at the product in the reaction we just talked about. It has a chirality center and therefore can exist as two enantiomers:The question is which one forms in excess, or in other words what is the stereochemistry of this, and in general, for the electrophilic addition reactions of alkenes. And this what we will discuss in today' post.Addition Reactions that Form a Product with One Chirality CenterThere are two possible scenarios for the starting alkene that we can have;1) the starting material alkene has no chiral centers2) there is a chiral center in the alkene. Let's start with the first option.Addition to an alkene with no stereogenic center For example, draw the major product(s) of the following reaction:For the regiochemistry, we know that according to the Markovnikov's rule, the Br will be added to the more substituted carbon:Notice that the carbon where the Cl had added became a chiral center, therefore we need to address whether it has an R or S absolute configuration. And the answer is that it actually is a racemic mixture of R and S enantiomers.This is explained by the fact that carbocations are sp2-hybridized, flat centers (we are talking about the positively charged carbon) and the nucleophilic attack occurs from both sides:This attack happens in the same amounts and as a result, a racemic mixture of two enantiomers is obtained.To summarize, addition reactions of alkenes with no stereogenic center that form a product with one stereogenic center produce a racemic mixture of enantiomers.Scenario 2 – Addition to an alkene with a stereogenic center If the starting alkene contains a chirality center, and the addition to the double bond creates a new chirality center, then the products are diastereomers:The asymmetric center in the starting material is not changed since it does not participate in the reaction. The new asymmetric center, however, is opposite for each product depending on the face the bromide had attacked the carbocation.Therefore, the products are a mixture of diastereomers. Similar to this, SN1 reactions can also produce diastereomers even though we usually say that they give a racemic mixture. You can check problems 3.5 and 3.6.Addition Reactions that Form a Product with Two Chirality Centers Let's consider the reaction of 1,2-dimethylcyclohexene with HBr. The starting material does not have any asymmetric centers. However, it produces four stereoisomers in this reaction!Let's see how this happens and what is the relationship between these stereoisomers. The first step is, as usual, the protonation of the double bond and what is important here is to remember/visualize that the H can add from both faces of the double bond:Notice that because of the hydrogen adding from different faces, the new chirality canter can be either R or S, and statistically it forms in a 50:50 ratio. There is no preference as to hydrogen adding from one side or the other side – no stereoselectivity.Similar to this, once the carbocation is formed, the bromide ion attacks the positively charged, trigonal planar carbon from above or below. This variety of additions results in four stereoisomers as final products.These are pairs of enantiomers and each enantiomer has two diastereomers:There is no control on the stereochemistry of this reaction and the proton, as well as the bromide (or any other substituent), add from both sides in equal amounts. Therefore, the reaction is not stereoselective i.e. none of the stereoisomers is formed preferentially. It is also not stereospecific, as the same products are obtained regardless if the cis or trans stereoisomers of the alkene are used.Therefore, when two stereogenic centers are formed in an addition reaction of alkenes, all the possible stereoisomers are formed, and the product is a mixture of enantiomers and diastereomers.Syn and Anti Additions to AlkenesLabeling the addition as "Above" and "Below" is not scientific and not accurate either as the direction depends on the viewer. Therefore, a more universal approach is used to describe the stereochemistry of additions to the double bond. When two groups add to the same side of the double bond, it is called a syn addition and when they add from different sides, it is an anti addition.A representative example of a syn addition to alkenes would be the hydroboration-oxidation reaction where the H and OH groups are adding to the same side of the double bond. The reaction, however, is going with a different mechanism; there are no ionic intermediates and it is a concerted mechanism:And a good example of an anti addition is the dihydroxylation reaction by peroxyacids.Notice how the H and OH groups appear on opposite sides in the product.These, of course, are not the only examples of syn and anti addition reactions to alkenes. You can find more examples from the list below. 1.Draw the intermediates and predict the main product(s) considering the stereochemistry for each of the following reactions: a) b) c) d) e) f) g) This article does not cite any sources. Please help improve this article by adding citations to reliable sources. Unsourced material may be challenged and removed.Find sources: "Syn and anti addition" – news · newspapers · books · scholar · JSTOR (December 2009) (Learn how and when to remove this template message) In organic chemistry, syn and anti addition are different ways in which two substituents can be added to a double bond or triple bond. This article will use cycloalkenes as examples. Syn addition is the addition of two substituents to the same side (or face) of a double bond, resulting in a decrease in bond order but an increase in number of substituents. Generally the substrate will be an alkene or alkyne. An example of syn addition would be the oxidation of an alkene to a diol via a suitable oxidizing agent such as osmium tetroxide, OsO4, or potassium permanganate, KMnO4. Anti addition is in direct contrast to syn addition. In anti addition, two substituents are added to opposite sides (or faces) of a double bond or triple bond, once again resulting in a decrease in bond order and increase in number of substituents. The classical example of this is bromination (any halogenation) of alkenes. Depending on the substrate double bond, addition can have different effects on the molecule. After addition to a straight-chain alkene such as C2H4, the resulting alkane will rapidly and freely rotate around its single sigma bond under normal conditions (i.e. room temperature). Thus whether substituents are added to the same side (syn) or opposite sides (anti) of a double can usually be ignored due to free rotation. However, if chirality or the specific absolute orientation of the substituents needs to be taken into account, knowing the type of addition is significant. Unlike straight-chain alkenes, cycloalkene syn addition allows stable addition of substituents to the same side of the ring, where they remain together. The cyclic locked ring structure prevents free rotation. Syn elimination and anti elimination are the reverse processes of syn and anti addition. These result in a new double bond, such as in Ei elimination. External links IUPAC, Compendium of Chemical Terminology, 2nd ed. (the "Gold Book") (1997). Online corrected version: (2006–) "endo, exo, syn, anti". doi:10.1351/goldbook.E02094 Retrieved from " An addition reaction, in organic chemistry, is in its simplest terms an organic reaction where two or more molecules combine to form a larger one (the adduct).[1][2] Addition reactions are limited to chemical compounds that have multiple bonds, such as molecules with carbon–carbon double bonds (alkenes), or with triple bonds (alkynes), and compounds that have rings, which are also considered points of unsaturation. Molecules containing carbon—hetero double bonds like carbonyl (C=O) groups, or imine (C=N) groups, can undergo addition, as they too have double-bond character. An addition reaction is the reverse of an elimination reaction. For instance, the hydration of an alkene to an alcohol is reversed by dehydration. There are two main types of polar addition reactions: electrophilic addition and nucleophilic addition. Two non-polar addition reactions exist as well, called free-radical addition and cycloadditions. Addition reactions are also encountered in polymerizations and called addition polymerization. General overview of addition reactions. Top to bottom: electrophilic addition to alkene, nucleophilic addition of nucleophile to carbonyl and free-radical addition of halide to alkene Depending on the product structure, it could promptly react further to eject a leaving group to give the addition–elimination reaction sequence. References ^ Morrison, R. T.; Boyd, R. N. (1983). Organic Chemistry (4th ed.). Boston: Allyn and Bacon. ISBN 0-205-05838-8. ^ March, Jerry (1985), Advanced Organic Chemistry: Reactions, Mechanisms, and Structure (3rd ed.), New York: Wiley, ISBN 0-471-85472-7. Wikiquote has quotations related to Addition reaction. Retrieved from "

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